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Poly(di-*n*-alkylsilylene) Copolymers: Investigation of the Microstructure by ^{1}H and ^{29}Si Solution NMR and Pyrolysis–Gas Chromatography/Mass Spectroscopy

Rogério Menescal, Jeffrey Eveland, and Robert West*

Department of Chemistry, University of Wisconsin—Madison, Madison, Wisconsin 53706

Marianne Blazsó

Research Laboratory for Inorganic Chemistry, Hungarian Academy of Sciences,
H-1112 Budapest, Budaörsi út 45 Hungary

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ABSTRACT: Thirteen copolymers of the type $(R_2Si)_n(R'_2Si)_m$ have been synthesized, where R, R′ = *n*-hexyl, *n*-pentyl, *n*-butyl, *n*-propyl, ethyl, and methyl, and R ≠ R′. The ^{1}H and ^{29}Si solution NMR spectra and thermal (DSC) transitions were measured for the copolymers and compared with those for the corresponding homopolymers. The composition (*n*/*m* ratio) was obtained from solution NMR and pyrolysis–GC/MS. The distribution of comonomers along the polymer backbone was determined by calculations from the pyrolysis–GS/MS results and found to be mostly random in nature.

I. Introduction

In the past 13 years there has been abundant research on the synthesis and characterization of polysilanes with a number of different alkyl and aryl substituents either symmetrically or asymmetrically substituted.[1]

Besides numerous homopolymers, $(R_2Si)_n$ or $(RR'Si)_n$, many copolymers $(R_2Si)_n(RR'Si)_m$,[1a] have been described. Copolymers with an alternating sequence of monomer units along the polymer chain have been prepared by sodium condensation of dihalotrisilanes,[2,3] $XSiR_2$—SiR'_2—SiR_2X, or by anionic polymerization of "masked disilenes".[4,5] Partially ordered copolymers have also been made by condensation of unsymmetrical disilanes, ClR_2Si—$SiRR'Cl$.[4,6] However most copolymers have been made by condensing two different dichlorosilanes, R_2SiCl_2 and R'_2SiCl_2.

In characterizing polysilane copolymers, it is important first of all to determine their composition, that is, the *n*/*m* ratio in $(R_2Si)_n(R'_2Si)_m$. In favorable cases, this can be determined by ^{1}H NMR spectroscopy. Information about the distribution of comonomer units along the polymer chain is also desirable. For elucidating the microstructure, ^{13}C and ^{29}Si NMR spectra in solution have proved useful.[6-8] In addition, pyrolysis–GC/MS can be a valuable tool in determining the distribution of monomeric units along the backbone, especially when they are too similar to be distinguished in the ^{1}H, ^{13}C, or ^{29}Si solution NMR spectra of the copolymer (e.g. *n*-Hex_2Si and *n*-Pen_2Si units in $(n\text{-}Hex_2Si)_n(n\text{-}Pen_2Si)_m$). So far only a few polysilylene copolymers have been analyzed by this method.[8-12]

The elucidation of the structure and description of physical properties of the first few members of the di-*n*-alkyl symmetrically substituted homopolymers,[9,13-22] has been followed by an increased interest in their corresponding copolymers.[7,23-26] In this paper we report the synthesis of symmetric di-*n*-alkyl substituted copolymers and the study of their microstructure by ^{1}H and ^{29}Si solution NMR and by pyrolysis–GC/MS. The results obtained by the two methods are compared and discussed.

II. Results and Discussion

(a) Synthesis. The 13 di-*n*-alkylsilylene copolymers which were synthesized are listed in Table 1. Molecular weights, measured by gel permeation chromatography, ranged from 287 000 to 1 200 000 and yields were between 10 and 25%. The polymerizations were done by the common Wurtz procedure where the comonomers were introduced simultaneously and rapidly into a sodium dispersion in refluxing toluene. In a number of polymerization reactions with di-*n*-alkyldichlorosilanes we have found that high concentrations and fast addition of monomer (as opposed to the usual dropwise addition) yields monomodal distributions of high molecular weight polysilanes. Monomodal distributions were thus obtained in all reactions, except the ones where dichlorodimethylsilane was a comonomer, in which cases the polymers were bimodal. For the latter polymers, $(R_2Si)_n(Me_2Si)_m$ (R = *n*-hexyl, *n*-pentyl, *n*-butyl), the high (**5H**, **9H**, and **12H** in Table 1) and low (**5L**, **9L**, and **12L**) molecular weight fractions were easily separated by fractional precipitation from toluene with 2-propanol.

For the polymers containing Me_2Si groups, the large difference in reactivity of the comonomers tended to promote the formation of blocks. When large amounts of Me_2Si units were present, the copolymers became insoluble in toluene (the homopolymer $[Me_2Si]_n$ is insoluble); therefore the feed ratio was varied in order to obtain only soluble material. A feed ratio of *n*-Hex_2SiCl_2/Me_2SiCl_2 = 1.5 resulted in 15% yield of a completely soluble polymeric product, $(n\text{-}Hex_2Si)_n(Me_2Si)_m$ (**14**) with a bimodal distribution (MW = 1.40×10^6, MW = 1.58×10^3, and *n*/*m* = 2.51, according to ^{1}H solution NMR). The high ratio suggests the existence of long blocks of *n*-Hex_2Si units, which is manifest in the microphase segregation observed by wide angle X-ray diffraction (Figure 1). When the comonomer feed ratio was 1.0, an insoluble fraction was obtained (probably with long blocks of Me_2Si units) along with a small soluble fraction. With a ratio of 1.3 we were able to obtain a totally soluble bimodal polymeric product (**5H** and **5L**), which was fractionated and characterized. Results similar to ours, with a 1.0 feed ratio, were also obtained by Schilling,[7] that is, an insoluble polymer fraction and a bimodal soluble fraction. The synthesis of poly(dimethylsilylene-*co*-di-*n*-hexylsilylene) had been re-

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Table 1. Polysilane Random Copolymers, $(R_2Si)_n(R'_2Si)_m$

polymer	R	R′	$10^{-3}M_w$	M_w/M_n	yield (%)	feed ratio[a]	n/m[b] ^1H	n/m[b] ^{29}Si	n/m Py–GC/MS
1	n-hexyl	n-pentyl	461	2.9	25	1.0			0.39
2	n-hexyl	n-butyl	1220	1.6	8	1.0	0.84		0.58
3	n-hexyl	n-propyl	351	2.4	13	1.0	0.76	0.75	0.66
4	n-hexyl	ethyl	435	2.7	18	1.8	1.11	1.16	0.60
5H	n-hexyl	methyl	395	2.1	17[c]	1.3	1.33	1.18	0.72
5L			6	1.5			0.32		0.20
6	n-pentyl	n-butyl	680	2.6	17	1.0	0.89		0.82
7	n-pentyl	n-propyl	430	4.2	21	1.0	0.98	0.96	0.89
8	n-pentyl	ethyl	400	3.3	14	1.5	0.81	0.90	0.86
9H	n-pentyl	methyl	592	2.4	19[c]	2.0	1.30		1.36
9L			25	1.8			0.89		0.98
10	n-butyl	n-propyl	340	5.3	11	1.0	1.45	1.5	1.46
11	n-butyl	ethyl	287	4.3	13	1.5	0.87	0.80	0.79
12H	n-butyl	methyl	844	1.8	21[c]	2.0	2.19		2.27
12L			26	1.3			0.79		0.89
13	n-propyl	ethyl	14	2.2	21	1.0	0.83	0.85	0.87

[a] R_2SiCl_2/R'_2SiCl_2. [b] From NMR spectra. [c] Overall yield of polymer with a bimodal molecular weight distribution.

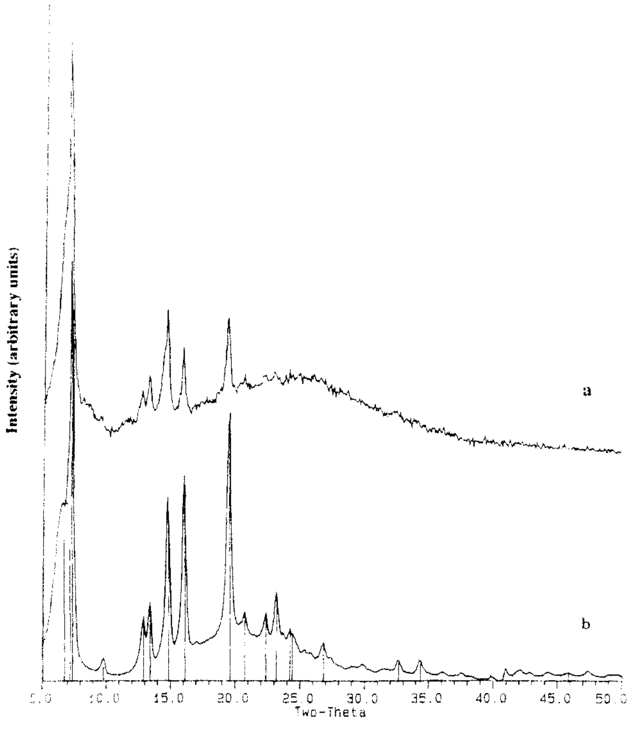

Figure 1. Powder X-ray diffraction of (a) $(n\text{-}Hex_2Si)_n(n\text{-}Me_2Si)_m$ (14) and (b) $(n\text{-}Hex_2Si)_n$.

ported previously without reference to its composition or sequential distribution of comonomers.[3,4] In the case of $(n\text{-}Bu_2Si)_n(Me_2Si)_m$ a comonomer feed ratio of $n\text{-}Bu_2SiCl_2/Me_2SiCl_2$ of 0.5 formed an insoluble copolymer with Me_2Si blocks. When the feed ratio was 1.0, a soluble copolymer with $n/m = 0.5$ was obtained together with insoluble polymeric material, and finally, when the feed ratio was 2.0, only soluble copolymer (**12H** and **12L**) was obtained.

The n/m ratios shown in Table 1 were determined from integration of the ^{29}Si NMR spectra (Figures 2–4) and the methyl proton peaks of the ^1H NMR spectra (Figure 5 and 6). For copolymer $(n\text{-}Hex_2Si)_n(n\text{-}Pen_2Si)_m$ (**1**) the resonances are unresolved in both spectra; in this polymer n/m is probably near the feed ratio, 1.0. Copolymers **2** and **6** also have comonomer units which are so similar that their respective peaks could not be completely resolved in the ^{29}Si NMR, but unlike copolymer **1**, they have well-resolved proton resonances (Figure 5), which were used to determine n/m.

The ^{29}Si NMR spectra of copolymers **9H**, **9L**, **12H**, and **12L** were obtained using an INEPT pulse sequence with parameters optimized for the Me_2Si units, and therefore the relative areas of the peaks are not representative of the n/m ratio; here again integration of the resonances in the ^1H NMR spectra was used to determine n/m.

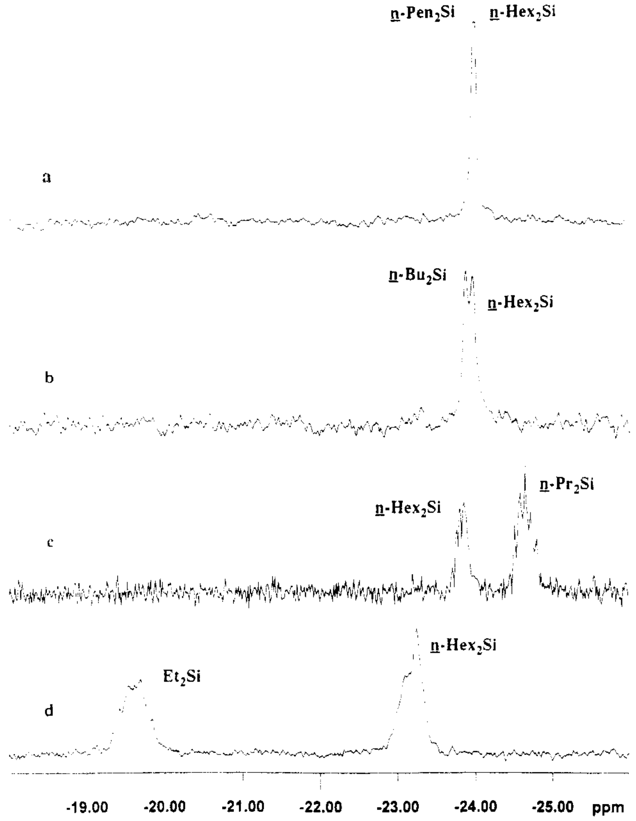

Figure 2. ^{29}Si NMR spectra of $(n\text{-}Hex_2Si)_n(R_2Si)_m$ in benzene-d_6, where R = (a) n-pentyl, (b) n-butyl, (c) n-propyl, and (d) ethyl.

(b) ^{29}Si NMR Spectra. The ^{29}Si NMR chemical shifts for all copolymers are shown in Table 2. For copolymers containing Me_2Si units (**5H**, **9H**, and **12H**) the peaks were easily assigned from the chemical shifts of the corresponding homopolymers (Table 3). For copolymers **3**, **6**, **7**, and **10** a second polymerization with a different comonomer feed ratio was performed in order to positively assign the peaks. Copolymers **4**, **8**, **11**, and **13**, which contain Et_2Si units, all have a peak around −19 ppm, far downfield from other resonances observed for these polymers. This peak was assigned to the Et_2Si silicons. Corresponding to this, poly(diethylsilylene) shows the most downfield chemical shift in the solid state ^{29}Si NMR of all polysilanes reported to date (−21.2 ppm). The peaks in copolymer **2** (Figure 2) were assigned on the basis of the

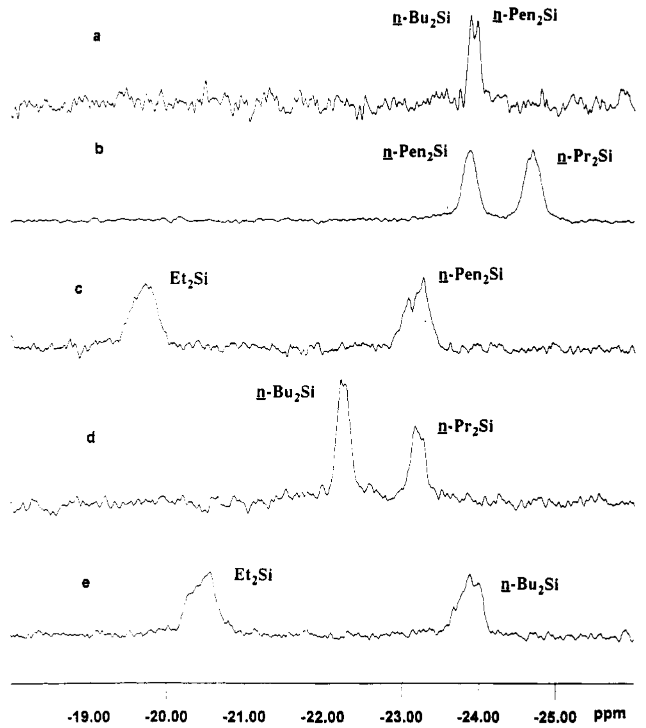

Figure 3. ^{29}Si NMR spectra of $(n\text{-Pen}_2\text{Si})_n(\text{R}_2\text{Si})_m$, with R = (a) n-butyl, (b) n-propyl, and (c) ethyl and of $(n\text{-Bu}_2\text{Si})_n(\text{R}_2\text{Si})_m$, with R = (d) n-propyl and (e) ethyl.

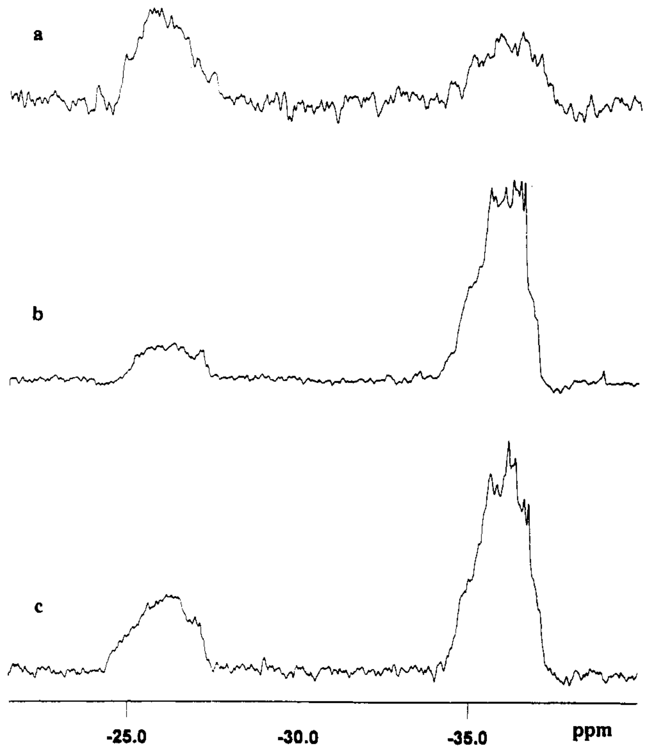

Figure 4. ^{29}Si NMR spectra of the high molecular weight fractions of $(\text{R}_2\text{Si})_n(\text{Me}_2\text{Si})_m$, where R = (a) n-hexyl, (b) n-pentyl, and (c) n-butyl.

intensities of the CH_3 peaks of n-Hex_2Si and n-Bu_2Si units in the ^{1}H NMR spectrum (Figure 5), as described below. The relative position of the chemical shifts of the two silylene units in the ^{29}Si NMR is the same as in the homopolymers, with $(n\text{-Hex}_2\text{Si})_n$ upfield from $(n\text{-Bu}_2\text{Si})_n$.

The copolymers show ^{29}Si NMR line widths much broader than those of the soluble homopolymers, as is evident from Table 3 and the spectra in Figures 2–4. As the difference between the length of the two different alkyl substituents of the copolymers increases, the peaks become broader and move apart. Fine structure can be observed in some spectra, for instance that of $(n\text{-Hex}_2\text{Si})_n(n\text{-Pr}_2\text{Si})_m$, but in most of them the chemical shift differences due to various comonomer sequences are unresolved. The absence of any sharp predominant peaks in all spectra indicates that there are no long blocks of any specific silylene unit.[27]

The relative positions of the peaks in the ^{29}Si NMR spectra in solution vary with the length of the alkyl group. For the homopolymers $(n\text{-Hex}_2\text{Si})_n$, $(n\text{-Pen}_2\text{Si})_n$, and $(n\text{-Bu}_2\text{Si})_n$ the peaks move slightly downfield as the length of the alkyl group decreases (Table 3). This trend is maintained in copolymers **2** and **6** (Table 2). Since $(n\text{-Pr}_2\text{Si})_n$ $(\text{Et}_2\text{Si})_n$ are insoluble, there are no solution ^{29}Si NMR data available, but in copolymers **3**, **7**, and **10** the n-Pr_2Si units are always the more upfield, thus reversing the above mentioned trend. In copolymers **4**, **8**, **11**, and **13** the resonances for the Et_2Si units are always the more downfield, and in copolymers **5H**, **9H**, and **12H** the $\text{Me}_2{}^{29}\text{Si}$ resonances are always the more upfield. This places the ^{29}Si chemical shifts in the order $\text{Et}_2\text{Si} > n\text{-Bu}_2\text{Si} > n\text{-Pen}_2\text{Si} > n\text{-Hex}_2\text{Si} > n\text{-Pr}_2\text{Si} > \text{Me}_2\text{Si}$. Interestingly, the solid state ^{29}Si NMR chemical shifts of homopolymers which crystallize in an all-*trans* conformation follow the same order, that is, $(\text{Et}_2\text{Si})_n > (n\text{-Hex}_2\text{Si})_n > (n\text{-Pr}_2\text{Si})_n > (\text{Me}_2\text{Si})_n$ (Table 3).

(c) ^{1}H NMR Spectra. Assignment of peaks for the n-hexyl, n-pentyl, and n-butyl groups was based on the solution spectra of the corresponding homopolymers.[28] The assignments for $(n\text{-Hex}_2\text{Si})_n(n\text{-Bu}_2\text{Si})_m$ (Figure 5) show that copolymerization shifted the NMR peaks of the two different R_2Si units in opposite directions, when compared to their respective homopolymers. In homopolymers $(n\text{-Hex}_2\text{Si})_n$ and $(n\text{-Bu}_2\text{Si})_n$ the methyl groups of the n-butyl and n-hexyl side chains resonate at 1.14 and 1.06 ppm, respectively, while in copolymer $(n\text{-Hex}_2\text{Si})_n(n\text{-Bu}_2\text{Si})_m$ the corresponding resonances are at 1.16 and 1.01 ppm. A similar phenomenon occurred also for other copolymers, where all peaks from the longer alkyl substituent were shifted upfield and all peaks from the shorter alkyl substituents were shifted downfield in relation to the resonances of the corresponding homopolymers. This shift in opposite directions greatly facilitated integration of the peak areas for determination of n/m.

Since $(n\text{-Pr}_2\text{Si})_n$ and $(\text{Et}_2\text{Si})_n$ are insoluble, their ^{1}H NMR spectra could not be obtained and the peaks for the propyl and ethyl side chains in the copolymers were assigned by subtraction of the ones from the hexyl, pentyl, and butyl groups, known from the spectra of $(n\text{-Hex}_2\text{Si})_n$, $(n\text{-Pen}_2\text{Si})_n$, and $(n\text{-Bu}_2\text{Si})_n$. For example, in copolymer $(n\text{-Pen}_2\text{Si})_n(n\text{-Pr}_2\text{Si})_m$ (Figure 6b) the peaks of the pentyl group can be easily identified from the spectra of the corresponding homopolymer (Figure 6a), and by subtraction of these, the peaks for the propyl substituent were assigned. A similar approach was used to identify all peaks in copolymers **3**, **4**, **8**, **10**, and **11**, which contain either n-propyl or ethyl side chains. The resonances in the ^{1}H NMR spectrum of the soluble copolymer $(n\text{-Pr}_2\text{Si})_n(\text{Et}_2\text{Si})_m$[9] were also good references for assigning the peaks of propyl and ethyl units in those copolymers, since they provide a good indication of the hypothetical positions of the chemical shifts of homopolymers $(n\text{-Pr}_2\text{Si})_n$ and $(\text{Et}_2\text{Si})_m$ in solution.

All proton resonances of the copolymers were found to be downfield from 1 ppm, except those of the Me_2Si units. In copolymers **5**, **9**, and **12**, the Me_2Si resonances appeared as broad peaks, centered about 0.60 and 0.35 ppm for the high and low molecular weight fractions, respectively. Such values are within the range observed in the ^{1}H NMR, for polymers with Me_2Si units. The chemical shift of oligomeric $(\text{Me}_2\text{Si})_n$ ($n \cong 30$),[29] shows a broad peak between

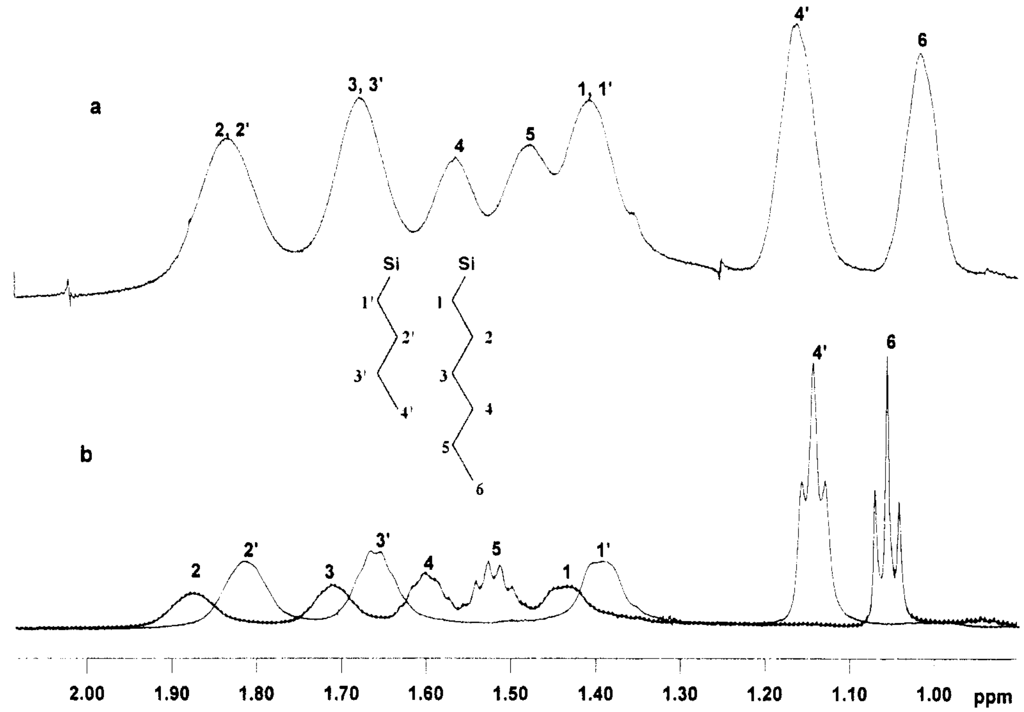

Figure 5. ^{1}H NMR spectra of (a) $(n\text{-Hex}_2\text{Si})_n(n\text{-Bu}_2\text{Si})$ and (b) $(n\text{-Hex}_2\text{Si})_n$ and $(n\text{-Bu}_2\text{Si})_n$.

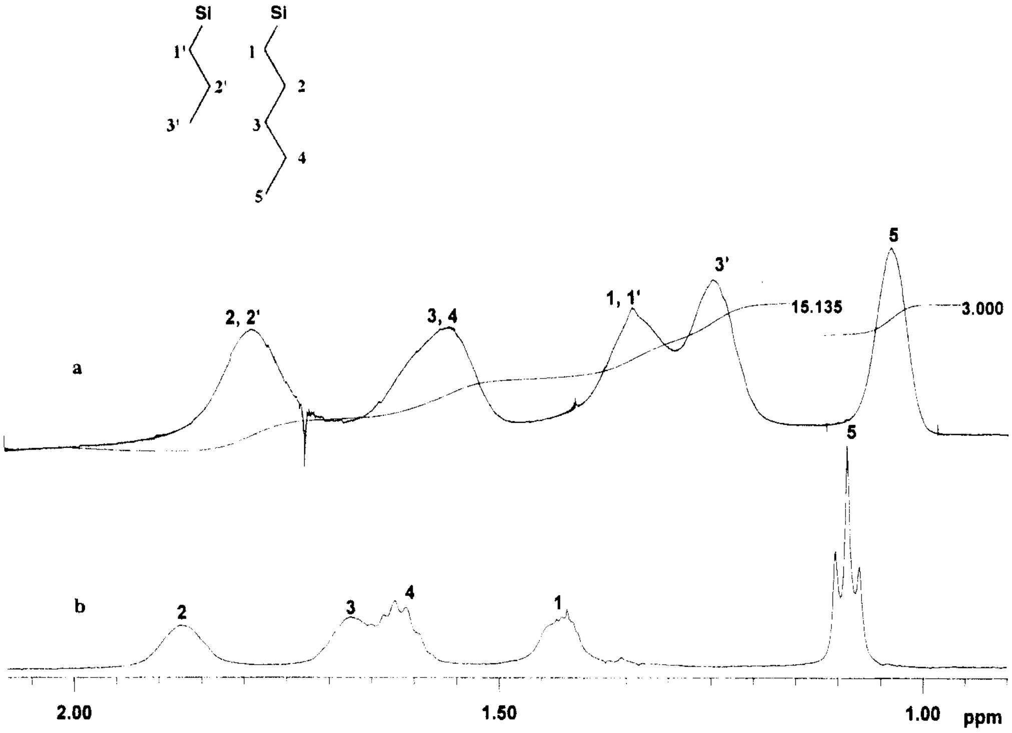

Figure 6. ^{1}H NMR spectra of (a) $(n\text{-Pen}_2\text{Si})_n(n\text{-Pr}_2\text{Si})_m$ and (b) $(n\text{-Pen}_2\text{Si})_n$.

0.14 and 0.25 ppm, and a number of different copolymers with Me_2Si units have their methyl resonances reported between 0.1 and 0.5 ppm.[30]

Except for $(n\text{-Hex}_2\text{Si})_n(n\text{-Pen}_2\text{Si})_m$ (1), the n/m ratio was found by integrating the area of the methyl peaks, which were upfield from the methylene ones in all copolymers (Figure 5 and 6). For copolymers 2 (Figure 5), **5H**, **5L**, **6**, **9H**, **9L**, **10**, **12H**, and **12L** the peaks from the two methyl groups were completely resolved from all others and n/m was easily obtained from the ratio of their areas. For copolymers **3**, **4**, **7** (Figure 6b), **8**, **11**, and **13**, however, only one of the methyl peaks was completely resolved from all others, the one from the longest alkyl substituent. In those cases the n/m ratio was obtained by integration of the area of the resolved methyl peak and subtraction of the area corresponding to the remaining protons of that substituent from the area of all other peaks. For example in copolymer 7 (Figure 6b), the methyl peak of the pentyl substituent was completely resolved from all others but the methyl peak of the propyl group was not. Since the value for the integration of the methyl peak of the pentyl substituent is 3, the value for the integration of the methylene protons should be equal to 8. Subtraction of 8 from 15.135 gives 7.135, which is the integration value for the protons of the propyl substituent. For $n/m = 1$ the pentyl to propyl integration ratio is 11/7; therefore Pen/Pr = 11/7.135 gives us $n/m = 0.98$.

(d) Pyrolysis–Gas Chromatography/Mass Spectroscopy. The composition of the copolymer (n/m ratio in Table 1) and the distribution of the two different

Table 2. ^{29}Si NMR Chemical Shifts of Copolymers $(R_2Si)_n(R'_2Si)_m$ in benzene-d_6 at 25 °C

polymer	R	R′	δ (ppm) $R_2{}^{29}Si$	 $R'_2{}^{29}Si$
1	*n*-hexyl	*n*-pentyl	−23.97	−23.97
2	*n*-hexyl	*n*-butyl	−23.91	−23.86
3	*n*-hexyl	*n*-propyl	−23.83	−24.63
4	*n*-hexyl	ethyl	−23.25	−19.72
5H	*n*-hexyl	methyl	−25.80	−36.20
6	*n*-pentyl	*n*-butyl	−23.99	−23.90
7	*n*-pentyl	*n*-propyl	−23.92	−24.71
8	*n*-pentyl	ethyl	−23.26	−19.74
9H	*n*-pentyl	methyl	−26.50	−36.80
10	*n*-butyl	*n*-propyl	−22.28	−23.21
11	*n*-butyl	ethyl	−22.49	−19.17
12H	*n*-butyl	methyl	−26.30	−36.34
13	*n*-propyl	ethyl	−23.40	−19.12

Table 3. Solution (benzene-d_6) and Solid State ^{29}Si NMR Chemical Shifts of poly(di-*n*-alkylsilylene)s at Room Temperature

polymer	δ (ppm) solid state [ref]	 solution [ref]	$\Delta\nu_{1/2}$ (ppm)[a]
$(n\text{-}Hex_2Si)_n$	−21.5 [17]	−24.07	0.02
$(n\text{-}Pen_2Si)_n$	−26.3 [17]	−23.98	0.01
$(n\text{-}Bu_2Si)_n$	−25.5 [17]	−23.93	0.01
$(n\text{-}Pr_2Si)_n$	−23.7 [9]	insoluble	
$(Et_2Si)_n$	−21.2 [16]	insoluble	
$(Me_2Si)_n$	−34.45 [13b]	−37.4 [29]	0.07

[a] Peak width at half-maximum for solution data (1 ppm = 100.33 Hz).

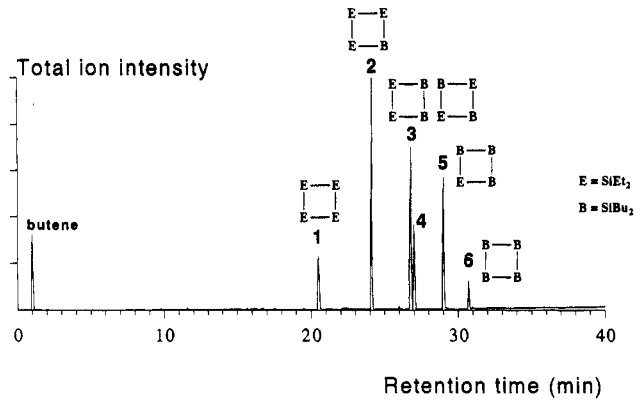

Figure 7. Pyrolysis–gas chromatogram showing four-membered rings from $(n\text{-}Bu_2Si)_n(Et_2Si)_m$: (1) octaethyl-, (2) hexaethyl-di-*n*-butyl, (3) 1,1,2,2-tetraethyl 3,3,4,4-tetra-*n*-butyl-, (4) 1,1,3,3-tetraethyl-2,2,4,4-tetrabutyl-, (5) diethylhexa-*n*-butyl-, and (6) octa-*n*-butylcyclotetrasilane.

Table 4. Quantitative Evaluation of the Pyrogram of Copolymer $(n\text{-}Bu_2Si)_n(Et_2Si)_m$ (11) in Figure 7

peak no.	relative molar amount cyclic	 *n*-Bu_2Si	 Et_2Si	relative occurrence [*n*-$Bu_2Si]_2$	 [*n*-Bu_2Si—$SiEt_2$]	 $[Et_2Si]_2$
1	11.3		11.3			11.3
2	29.6	7.4	22.2		14.8	14.8
3	22.8	11.4	11.4	5.7	11.4	5.7
4	12.2	6.1	6.1		12.2	
5	18.8	14.1	4.7	9.4	9.4	
6	5.3	5.3		5.3		
total (%)	100	44.3	55.7	20.4	47.8	31.8
n/m = 44.3/55.7 = 0.79						
calc relative occurrence of dyads for random $(n\text{-}Bu_2Si)_n(Et_2Si)_m$, with n/m = 0.79				19.5	49.3	31.2

Table 5. Relative Occurrence of Dyads in the Pyrolysis Products of $(R_2Si)_n(R'_2Si)_m$ Copolymers

polymer	n/m[a]	$[R_2Si—SiR_2]$ exp	 calc[b]	$[R_2Si—SiR'_2]$ exp	 calc[b]	$[R'_2Si—SiR'_2]$ exp	 calc[b]
1	0.39[c]	8	8	41	40	51	51
2	0.58[c]	15	14	44	47	41	40
3	0.66[c]	18	16	44	48	38	36
4	0.60[c]	13	14	49	47	38	39
5H	0.72[c]	17	18	50	49	33	34
5L	0.20[c]	2	3	28	28	69	69
6	0.82	22	20	45	49	32	30
7	0.89	22	22	50	50	28	28
8	0.86	22	1	48	50	30	29
9H	1.36	33	33	49	49	18	18
9L	0.98	24	25	51	50	26	26
10	1.46	35	35	48	48	17	17
11	0.79	20	19	48	49	32	31
12H	2.27	47	48	45	43	8	9
12L	0.89	20	22	54	50	26	28
13	0.87	21	22	51	50	28	29

[a] From pyrolysis–GC/MS. [b] Expected values assuming a random distribution of monomer units. [c] Values deviating by more than 0.1 from those evaluated from NMR peak areas.

monomeric units along the backbone were also studied by on line pyrolysis–gas chromatography/mass spectroscopy (py–GC/MS). While poly(dimethyl-*co*-di-*n*-alkylsilylene)s produced cyclic tetrasilanes and pentasilanes on pyrolysis, all other copolymers with substituents different than methyl gave off only tetramers. The cyclic silanes were separated by gas chromatography and identified by a coupled mass spectrometer. In Figure 7 the pyrogram for polymer $(n\text{-}Bu_2Si)_n(Et_2Si)_m$ shows the identified peaks for all possible cyclotetrasilanes obtained from pyrolysis of that copolymer. The n/m ratio and the experimental relative occurrence of dyads along the backbone were calculated from the relative amounts of different cyclic compounds, as illustrated in Table 4. The calculated relative occurrence of dyads for the assumed random copolymer $(n\text{-}Bu_2Si)_n(Et_2Si)_m$ with n/m = 0.79 was determined as shown below:

dyads	calcd relative occurrence
$[n\text{-}Bu_2Si]_2$	$\frac{0.79}{1.79} \times \frac{0.79}{1.79} \times 100 = 19.5$
$[n\text{-}Bu_2Si—SiEt_2]$	$2 \times \frac{0.79}{1.79} \times \frac{1.00}{1.79} \times 100 = 49.3$
$[Et_2Si]_2$	$\frac{1.00}{1.79} \times \frac{1.00}{1.79} \times 100 = 31.2$

The calculated and experimental values for the relative occurrence of dyads in all copolymers are summarized in Table 5. There is very good agreement between the two sets of data for almost all copolymers studied, thus indicating their random structural nature.

The pyrolysis and NMR n/m ratios are compared in Table 1. For copolymers 1 through 5L (Hex_2Si series) some disagreement between the n/m ratios obtained by the two different methods is evident. The differences probably result from the loss of higher molecular mass products due to cold spots in the pyrolyzer–gas chromatograph interface. These results show clearly the volatility limits of quantitative analysis by py–GC/MS. In spite of this limitation, the n/m ratio and the data on relative occurrence dyads were useful in determining the random nature of the copolymers.

A discussion of the mechanism of thermal decomposition and a detailed description of the pyrograms, mass spectra, and calculations are reported in a separate publication.[12]

(e) Differential Scanning Calorimetry. The homopolysilanes listed in Table 3 are known to be crystalline at 25 °C and to undergo a first-order thermal transition

Table 6. DSC First-Order Transition Temperatures (°C) for Copolymers $(R_2Si)_n(R'_2Si)_m$

copolymer	R	R′	T_{on}[a]	T_{peak}	T_{av}[b]	ΔT[c]	polymer	T_{on}	T_{peak}	ref
1	*n*-hexyl	*n*-pentyl	15	+23	48	33	$(n\text{-}Hex_2Si)_n$	43	50	34
2	*n*-hexyl	*n*-butyl	−20	−10	63	83	$(n\text{-}Pen_2Si)_n$	52	65	34
3	*n*-hexyl	*n*-propyl	−30	−16	145	175	$(n\text{-}Bu_2Si)_n$	79	84	
4	*n*-hexyl	ethyl	6	16	120	114	$(n\text{-}Pr_2Si)_n$	222	235	9
5H	*n*-hexyl	methyl	7	15	82	75	$(Et_2Si)_n$	207	224	14
6	*n*-pentyl	*n*-butyl	46	51	66	20	$(Me_2Si)_n$	131	157	34
7	*n*-pentyl	*n*-propyl	−12	6	138	150				
8	*n*-pentyl	ethyl	d		136					
9H	*n*-pentyl	methyl	0	17	86	86				
10	*n*-butyl	*n*-propyl	51	59	137	86				
11	*n*-butyl	ethyl	d		149					
12H	*n*-butyl	methyl	39	45	95	56				
13	*n*-propyl	ethyl	113	125	214	101				
14	*n*-hexyl	methyl	37	47	68	31				

[a] Onset of peaks. [b] Weighted average of T_{on} of corresponding homopolymers, calculated from the ^1H and ^{29}Si NMR copolymers n/m ratio. [c] $T_{av} - T_{on}$. [d] Only T_g detected.

above room temperature to a mesophase, in which conformational order is lost but interchain alignment still exists;[9,14,17,19,22] the exception is $(Me_2Si)_n$ which undergoes a transformation from one crystalline phase to another.[13b]

The crystallinity of copolymers in general is a function of the comonomer distribution along the chain.[31] The nature of such distribution (random, blocklike, alternating) is reflected in the melting point of the copolymers as compared to that of the respective homopolymers. Random copolymers usually have a much lower melting point than block copolymers of the same comonomer units. For the latter, the melting points are usually not far below the weighted average of the two homopolymers, while for the former the high degree of disorder along the backbone causes a much greater drop in the melting point.[32,33]

Table 6 shows the first-order transition temperatures for the 13 copolymers and their corresponding homopolymers, determined by differential scanning calorimetry (DSC). The onset temperature T_{on} for the thermal transition is listed for all polymers. For the copolymers, a weighted average onset temperature, T_{av}, was calculated from the n/m ratio and the onset temperature for the thermal transitions of the two homopolymers; ΔT is the difference between T_{av} and T_{on} for the copolymer. The values of ΔT (Table 6) show that the melting points of most copolymers are significantly lower than the weighted average of the melting points of the respective homopolymers, consistent with their random nature. The small ΔT's observed for polymers 1 and 6 reflect their higher crystallinity due to the similarity between substituent groups. As the relative difference in the length of the alkyl substituents increases (**10** and **13**), ΔT increases. The melting point of the blocklike copolymer $(n\text{-}Hex_2Si)_n(Me_2Si)_m$ (**14**) with $n/m = 2.5$, is 30 deg above that of random $(n\text{-}Hex_2Si)_n(Me_2Si)_m$ (**5H**) with $n/m = 1.33$, even though the latter is more abundant in units ($SiMe_2$) from the homopolymer with the higher transition temperature.

III. Summary

From ^1H and ^{29}Si NMR, py-GC/MS, and melting point data, the random nature of the copolymers in the $(R_2Si)_n(R'_2Si)_m$ family has been demonstrated. Unlike their corresponding homopolymers, most of the copolymers have first-order thermal transitions below room temperature. A detailed study of copolymer **13** has been described in ref 9 and additional data for the others will be reported in a separate publication.

IV. Experimental Section

(a) Synthesis. With the exception of dichlorodi-*n*-pentylsilane (bp = 102 °C/6 mmHg, which was prepared by addition of a THF solution of *n*-pentylmagnesium bromide to a THF solution of $SiCl_4$ (Hüls America, Inc.), all dichlorosilane monomers used were purchased from Hüls America, Inc. and distilled over potassium carbonate under nitrogen prior to use. Toluene was distilled from sodium and benzophenone ketyl under nitrogen gas and transferred to the reaction flask through a syringe. Sodium metal (99% from Aldrich Chemical Co., Inc.) was cut fresh under mineral oil, washed quickly with dry hexane and added to the reaction flask under a positive flow of argon, which was maintained at all times during setup and polymerization.

The method described below for the synthesis of poly(di-*n*-hexyl-*co*-di-*n*-propylsilylene) was used for the homopolymers $(R_2Si)_n$ where R = *n*-hexyl, *n*-pentyl, and *n*-butyl and all the copolymers listed in Table 1, except $(n\text{-}Pr_2Si)_n(Et_2Si)_m$.[9] The purity was determined by GPC, which showed no oligomers were present, and by infrared and ^{29}Si NMR spectroscopy, which showed no bands or signals from Si—O bonds.

Synthesis of Poly(di-*n*-hexyl-*co*-di-*n*-propylsilylene). A 250 mL three-necked ambered-glass round bottom flask was equipped with a Friedrichs condenser connected to an argon inlet. A mechanical stirring rod was attached to the center neck of the flask and a 25 mL pressure-equalized addition funnel was placed at the remaining neck after introduction of 3.37 g (0.146 mol, 2.05 equiv) of freshly cut sodium metal and 85 mL of dry toluene. Dichlorodi-*n*-propylsilane (6.50 mL, 0.0357 mol) and 10 mL (0.0357 mol) of dichlorodi-*n*-hexylsilane were syringed into the addition funnel. A sodium dispersion in toluene was prepared by stirring the metal for 15 min at high speed under reflux in toluene (oil bath at 125 °C). The comonomer mixture was added to the dispersion within 1 min and allowed to react for 2 h under reflux of toluene (the heat was withdrawn by lowering the oil bath during the addition). The reaction mixture was allowed to cool to ambient temperature, quenched with a slurry of sodium hydrogen bicarbonate in 2-propanol, and washed into a 1000 mL Erlenmeyer flask with a small volume of toluene. The oligomers were separated by precipitation of the salts and the polymer with 850 mL of 2-propanol. The salts and the precipitated copolymer were filtered off through a Büchner funnel and the solid mixture was stirred overnight in 200 mL of toluene to redissolve the copolymer. Once the copolymer was completely dissolved the salts were filtered and the polymer solution in toluene was washed three times with 50 mL of distilled water and dried over magnesium sulfate. The copolymer was then reprecipitated from toluene with 2000 mL of 2-propanol, filtered out, and dried under vacuum (0.02 Torr) at 100 °C for 3 h. Yield = 13%.

(b) Measurements. Molecular weights were measured by gel-permeation chromatography using a Water Associates Model 6000A liquid chromatograph equipped with three American Polymer Standards Corp. Ultrastyragel columns in series, with porosity indices of 10^3, 10^4, and 10^5 Å, and THF as eluant, with a flow of 1 mL/min. The polymers were detected with a Waters Model 440 ultraviolet absorbance detector at a wavelength of 254 nm and the data manipulated using a Waters Model 745 data module. Molecular weights were determined relative to a calibration from low polydispersity polystyrene standards.

^1H and ^{29}Si (100.33 MHz) NMR spectra were obtained on a Bruker AM-500 with 10% solutions of polymers in benzene-d_6

using $(CH_3)_4Si$ as reference. ^{29}Si NMR spectra for copolymers **9** and **12** were obtained using an INEPT pulse sequence. All other ^{29}Si NMR measurements were done using gated decoupling of protons and a relaxation delay of 50 s.

Pyrolysis–GC/MS measurements were performed in a Chemical Data Systems Pyroprobe 120, coupled to a Hewlett-Packard 5985B gas chromatograph–mass spectrometer, at 300 °C pyrolysis temperature in a helium atmosphere.

The X-ray diffractograms of poly(di-*n*-hexylsilylene) and copolymer **14** were obtained from films cast from hexane, dried in a vacuum oven for 12 h at 60 °C, on a Nicolet I2/V diffractometer, with a Cu Kα beam.

DSC measurements were performed with a 2910 TA Instruments and a 220 TA Instruments controller using mass samples of 10–11 mg in a dry helium atmosphere. Calibration was performed with mercury and indium. The measurements for the copolymers and $(\text{Bu}_2\text{Si})_n$ were performed from −100 to +250 °C at a heating rate of 10 °C/min after heating the samples to 200 °C at 200 °C/min and cooling to −100 °C at 10 °C/min.

(c) Proton NMR Assignments. ^{1}H NMR (ppm) assignments for homopolymers and copolymers (starred methyl and methylene (*) units belong to the shortest chain alkyl group) are as follows.

$(n\text{-Hex}_2\text{Si})_n$: 1.06 ($CH_3$, triplet, $^3J_{\text{H—H}} = 7.25$ Hz), 1.44 (—$^{\alpha}CH_2$—), 1.52 (—$^{\epsilon}CH_2$—, sextet), 1.60 (—$^{\delta}CH_2$—), 1.71 (—$^{\gamma}CH_2$—), 1.87 (—$^{\beta}CH_2$—).

$(n\text{-Pen}_2\text{Si})_n$: 1.09 ($CH_3$, triplet, $^3J_{\text{H—H}} = 7.25$ Hz), 1.43 (—$^{\alpha}CH_2$—), 1.62 (—$^{\delta}CH_2$—), 1.67 (—$^{\gamma}CH_2$—), 1.87 (—$^{\beta}CH_2$—).

$(n\text{-Bu}_2\text{Si})_n$: 1.14 ($CH_3$, triplet, $^3J_{\text{H—H}} = 7.00$ Hz), 1.39 (—$^{\alpha}CH_2$—), 1.66 (—$^{\gamma}CH_2$—, 1.81 (—$^{\beta}CH_2$—).

$(n\text{-Hex}_2\text{Si})_n(n\text{-Bu}_2\text{Si})_m$ (**2**): 1.01 (CH_3), 1.16 (CH_3*), 1.40 (—$^{\alpha}CH_2$—*), 1.48 (—$^{\epsilon}CH_2$—), 1.56 (—$^{\delta}CH_2$—), 1.67 (—$^{\gamma}CH_2$—, —$^{\gamma}CH_2$—*), 1.83 (—$^{\beta}CH_2$—, —$^{\beta}CH_2$—*).

$(n\text{-Hex}_2\text{Si})_n(n\text{-Pr}_2\text{Si})_m$ (**3**): 1.01 (CH_3), 1.30 (CH_3*), 1.41 (—$^{\alpha}CH_2$—, —$^{\alpha}CH_2$—*), 1.48 (—$^{\epsilon}CH_2$—), 1.57 (—$^{\delta}CH_2$—), 1.68 (—$^{\gamma}CH_2$—, 1.85 (—$^{\beta}\gamma CH_2$—, —$^{\beta}CH_2$—*).

$(n\text{-Hex}_2\text{Si})_n(\text{Et}_2\text{Si})_m$ (**4**): 1.00 (CH_3), 1.44 (CH_3*, —$^{\alpha}CH_2$—), 1.53 (—$^{\epsilon}CH_3$—), 1.58 (shoulder, —$^{\delta}CH_2$—), 1.65 (—$^{\gamma}CH_2$—), 1.83 (—$^{\beta}CH_2$—).

$(n\text{-Hex}_2\text{Si})_n(\text{Me}_2\text{Si})_m$ (**5H**): 0.70 (CH_3*), 1.00 (CH_3), 1.36 (shoulder, —αCH_2—), 1.48 (—$^{\delta}CH_2$—, —$^{\epsilon}CH_2$—), 1.61 (—$^{\gamma}CH_2$—), 1.79 (—$^{\beta}CH_2$—).

$(n\text{-Pen}_2\text{Si})_n(n\text{-Bu}_2\text{Si})_m$ (**6**): 1.07 (CH_3), 1.16 (CH_3*), 1.41 (—$^{\alpha}CH_2$—, —$^{\alpha}CH_2$—*), 1.60 (—$^{\delta}CH_2$—), 1.66 (—$^{\gamma}CH_2$—*), 1.83 (—$^{\beta}CH_2$—, —$^{\beta}CH_2$—*).

$(n\text{-Pen}_2\text{Si})_n(n\text{-Pr}_2\text{Si})_m$ (**7**): 1.04 (CH_3), 1.25 (CH_3*), 1.34 (—$^{\alpha}CH_2$—, —$^{\alpha}CH_2$—*), 1.56 (—$^{\gamma}CH_2$—, —$^{\delta}CH_2$—), 1.78 (—$^{\beta}CH_2$—, —$^{\beta}CH_2$—*).

$(n\text{-Pen}_2\text{Si})_n(\text{Et}_2\text{Si})_m$ (**8**): 1.01 (CH_3), 1.35 (CH_3*, —$^{\alpha}CH_2$—, 1.42 (—$^{\alpha}CH_2$—*), 1.53 (—$^{\gamma}CH_2$—, —$^{\delta}CH_2$—), 1.77 (—$^{\beta}CH_2$—).

$(n\text{-Pen}_2\text{Si})_n(\text{Me}_2\text{Si})_m$ (**9H**): 0.61 (CH_3*), 1.06 (CH_3), 1.39 (—$^{\alpha}CH_2$—), 1.59 (—$^{\gamma}CH_2$—, —$^{\delta}CH_2$—), 1.61 (—$^{\gamma}CH_2$—), 1.82 (—$^{\beta}CH_2$—).

$(n\text{-Bu}_2\text{Si})_n(n\text{-Pr}_2\text{Si})_m$ (**10**): 1.13 (CH_3), 1.27 (CH_3*), 1.38 (—$^{\alpha}CH_2$—*), 1.64 (—$^{\gamma}CH_2$—), 1.81 (—$^{\beta}CH_2$—, —$^{\beta}CH_2$—*).

$(n\text{-Bu}_2\text{Si})_n(\text{Et}_2\text{Si})_m$ (**11**): 1.07 (CH_3), 1.33 (—$^{\alpha}CH_2$—, —$^{\alpha}CH_2$—*, CH_3*), 1.57 (—$^{\gamma}CH_2$—), 1.73 (—$^{\beta}CH_2$—).

$(n\text{-Bu}_2\text{Si})_n(\text{Me}_2\text{Si})_m$ (**12H**): 0.75 (CH_3*), 1.10 (CH_3), 1.33 (—$^{\alpha}CH_2$—), 1.61 (—$^{\gamma}CH_2$—), 1.76 (—$^{\beta}CH_2$—).

$(n\text{-Pr}_2\text{Si})_n(\text{Et}_2\text{Si})_m$ (**13**): 1.20 (CH_3, triplet, $^3J_{\text{H}}—H = 6.5$ Hz), 1.31 (CH_3*), 1.34 (—$^{\alpha}CH_2$—, —$^{\alpha}CH_2$—*), 1.75 (—$^{\beta}CH_2$—).

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